THE FLUORESCENT AND ABSORPTION SPECTRA

OF

ANTHRACENE AND PHENANTHRENE VAPORS.

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By

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TABLE OF CONTENTS.

I. Introduction.

The fluorescence of vapors was first observed by Lommel[1] for iodine vapor in 1883. A few years later Ramsay and Young[2] and E. Wiedemann[3] found that some liquid solutions, when raised above their critical temperatures, fluoresce. Later, Wiedemann and Schmidt[4] discovered a long list of fluorescent organic vapors, among which was anthracene. They found that this vapor under the action of arc-light or sunlight fluoresced an intense blue, the fluorescent light lying, as a whole, on the red side of the region of maximum absorption. In 1896 they[5] discovered also that the metallic vapors of sodium and potassium are fluorescent. Quite recently Professor Wood[6] has made an extensive study of the fluorescence of sodium vapor. It has been shown by Hartley[7] that mercury vapor also is fluorescent under certain conditions.

With the exception of sodium none of these vapors had been investigated extensively for its fluorescence; and yet it seemed desirable that such work should be done, for the sake of the aid which it might afford for the solution of the problem of luminescence and ultimately of the problem of the nature of matter. In the present

1. Lommel, Wied. Annal. 19, 356, 1883.
2. Ramsay and Young, Chem. News 54, 203, 1886.
3. E. Wiedmenan, Wied Annal. 41, 209, 1890.
4. Wiedemann and Schmidt, Wied. Annal. 56, 18, 1895.
5. Wiedemann and Schmidt, Wied. Annal. 57, 447, 1896.
6. R. W. Wood, Phil. Mag. 10, 513, 1905.
7. Hartley, Roy. Soc. Proc. 76 A, 428, 1905.

investigation   the object was to study in more detail the fluorescence
of anthracene vapor, one of the very strongly fluorescent organic
vapors.

II. The Fluorescent Spectrum of Anthracene Vapor.
(a) Method and Apparatus.

The fluorescence of the anthracene vapor was first studied
by means of a small quartz spectrograph. The pure anthracene used
was obtained from the commercial product by distilling twice from
an excess of caustic potash and then crystallizing from benzene under
the action of sunlight. A few centigrams of the crystals were enclosed
in a crown-glass bulb (5 to 8 cms. in diameter) which was then evac-
uated and sealed.

The bulb was placed in a heating apparatus arranged as shown
in Fig. I. It was hung in a wire cage between the two side

Fig. I.
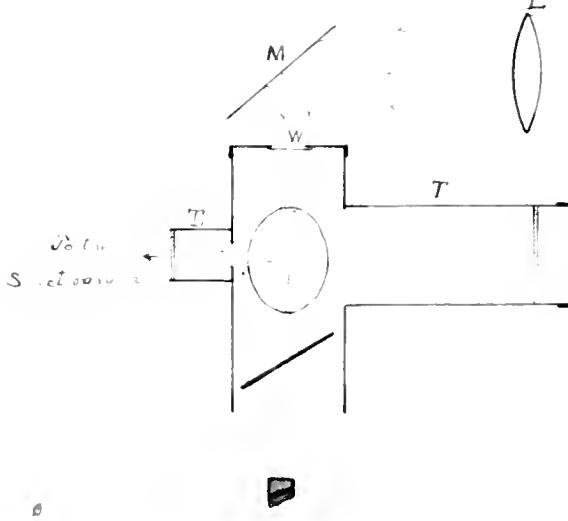
tubes, T_1 and T_2, in
such a manner that the
light employed to
excite fluorescence,
after passage through
the condensing lens ,L,
and reflection from the
mirror, M, downward
through the mica window,

W, was focused at the center of the bulb.

The tube, T, contained a rectangular opening at its inner end and a glass window near its outer end. When the bulb was heated and the anthracene made to fluoresce, the fluorescent light was examined by the spectrograph through this tube.

The larger tube, T_{1}, provided with a cap over its outer end, served a double role; first, as an observing tube for adjusting the apparatus so as to properly focus the light in the bulb, and secondly, as a dark background against which to observe the fluorescence through the other tube, T.

Care was taken always to adjust the bulb so that the cone of exciting light should be reflected from the bottom of the bulb straight back along its path. This was done in order to get rid, as far as possible, of the light scattered by reflection from the sides of the bulb. It was found, when bulbs of the proper size and shape were adjusted in this way, that an exposure of three hours, made for scattered light alone, gave a very faint photograph as compared with that of the fluorescent and scattered light combined.

Various sources of violet and ultraviolet light were tried, viz. the sun, the carbon and zinc arcs in air, the mercury, silver, and lead arcs in vacuo, and the cadmium, aluminium, copper, zinc

and magnesium sparks. Of these the carbon arc produced the most

intense fluorescence in the anthracene vapor and so was employed

almost exclusively. It was found that the fluorescence was due more

to the light from the incandescent gases between the carbons than

to the incandescent carbons themselves. Its intensity increased

or decreased with the intensity of the group of three cyanogen bands

in the violet.

(b) The Fluorescence.

When the bulb was heated until the anthracene began to

vaporize, the path of the arc-light through it was marked by a cone

of illuminated particles which scattered partially polarized white

light in all directions. Gradually this disappeared as the anthra-

cene became completely vaporized and was replaced by a cone of

brilliant blue fluorescent light in which no polarization could

be detected. Examined photographically with the quartz spectrograph

it gave a spectrum (Plate I) which extended continuously from

$365 \mu\mu$ to $470 \mu\mu$, but was crossed by three distinct bands at 390,

415 and $432 \mu\mu$. The same spectrum was also obtained when sunlight,

or light from any of the other sources, was employed as the exciting

light.

The range of the apparatus was from $325 \mu\mu$ to $540 \mu\mu$, the

limit in the ultraviolet being set by the crown glass of the bulb,

which is opaque to radiation of shorter wave-length than 325 $\mu\mu$.

The photograph did not show the slightest evidence of lines in the fluorescent spectrum. This, it was thought, might be due to the small resolving power of the quartz spectrograph in the region of the fluorescence, so a photograph was taken with a special, three-crown-prism spectrograph, designed by Professor Wood for his work on sodium vapor. The resolving power of this instrument was about fifteen times that of the quartz spectrograph; but in this case also the photograph failed to show any lines in the spectrum. The fluorescence was not intense enough to warrant the use of instruments of higher resolving power. It seems highly probable, however, that the fluorescent spectrum of anthracene vapor is not resolvable into lines like that of sodium vapor, but resembles, instead, the banded spectra of fluorescent liquids and solutions.

III. The Effect of Enclosing a Foreign Gas with the Anthracene.

To determine what effect upon the fluorescence the presence of another gas would have, the anthracene was enclosed in the bulb in turn with various gases at atmospheric pressure. It was found that some gases had practically no effect, while others extinguished the fluorescence more or less completely. The results are given in the following table:

Fluorescence of Anthracene Vapor.		
Not affected by	Extinguished by	Weakened by
Nitrogen	Cyanogen	Air
Hydrogen	Chlorine	
Illuminating gas	Sulphur dioxide	
Carbon monoxide	Oxygen	
Mercury vapor		
Carbon dioxide		

In the case of the gases listed in the first column of the table the quality of the fluorescence was unaffected by their introduction into the bulb. A slight decrease in intensity, however, was observed, due, probably, to the higher pressures in the bulb after the gases were introduced, (See $\S$ III). So far as could be ascertained none of these gases reacts chemically upon the anthracene vapor within the range of temperature set by the apparatus.

In the case of the gases listed in the second column the effect was practically to extinguish the fluorescence. Only the faintest trace, if any, of fluorescence could be observed when they were mixed with the anthracene. For these gases it was found that chemical action either began as soon as the temperature was raised

to a point where the anthracene was vaporized(this was the case with

cyanogen and chlorine), or at a temperature not much higher (this was

the case with sulphur dioxide and oxygen).It seemed highly probable

from this that the extinction of the fluorescence was due to some

sort of chemical influence.

That the chemical influence, if such it be, which affected

the fluorescence need not be such as to produce a permanent chemical

change in the anthracene was shown in the following way: A bulb

containing anthracene and oxygen was placed in an air-bath with a

similar bulb containing only anthracene. The temperature was then

raised just high enough to obtain strong fluorescence in the second

bulb. The first bulb was tested for fluorescence and found not to

show the slightest traces. It was then removed and the oxygen

pumped out and the bulb again placed in the bath and tested. The

fluorescence in this bulb was now found to be as brilliant as in

the other one. To find out if some of the anthracene had not been

acted upon and a consequent change in volume of the oxygen produced,

a bulb was used which terminated in a long capillary tube. The

oxygen was enclosed at atmospheric pressure, and, after subjecting

the bulb to the same heating as before, the end of the capillary

tube was broken off under mercury and the oxygen again brought

to atmospheric pressure. Not the slightest change in its volume

was observed. If any chemical action had occurred, it was evidently
of such a nature as to produce compensating changes in the volume
of the reacting substances. As this is highly improbable, we are
led to conclude that no reaction took place between the anthracene
                      that
and the oxygen, but‸whatever mutual action occurred produced effects
which lasted only while the given conditions of temperature and
mutual contact were maintained. During this time practically all
of the anthracene molecules must have been affected,for the extinct-
ion of the fluorescence was complete throughout the vapor.

The foregoing facts may be explained by assuming that, when
anthracene vapor is mixed with oxygen at a temperature not much
below that at which the two react chemically, there is a preliminary
grouping of the oxygen molecules about the anthracene molecules, or
vice versa, and that, while thus associated and before they rush
together into closer contact and form a new chemical compound,
the mutual forces are such as to prevent the anthracene molecules
from fluorescing, but are not great enough to bring about a reaction.
As thus considered the phenomenon is simply the first stage of the
reaction.
                                                          is
The effect of oxygen upon the anthracene vapor‸in many ways
similar to that of many liquid solvents upon the fluorescent sub-

8
stances dissolved in them.

When the vapor was mixed with air the fluorescence was much
weakened, becoming almost too weak to be seen when air at atmos-
pheric pressure,or greater,was used.   This weakening was easily
traceable to the oxygen contained in the air.

It seems highly probable from the foregoing facts that the
presence of foreign molecules,heavy or light, among the fluorescing
anthracene molecules does not have any app eciable effect upon the
fluorescence at ordinary pressures, except in those cases where a
chemical change, either incipient or permanent, occurs.

IV.   The Effect of Pressure.

In the experiment with the illuminating gas a thick-walled
glass bulb was employed and the pressure was varied from one
to twelve atmospheres. The visible fluorescence became less and
less intense as the pressure was increased, but was still per-
ceptible at the highest pressure. So far as this was tried with the
other gases the same results were obtained, an increase of pressure
in each case causing a diminution in the intensity of the fluorescence.

8. Kauffman & Beiswenger, Zeit. f. Phys. Chem. 50, 350, 1904.

The change in intensity was not very marked until the pressure exceeded one atmosphere. At all pressures below this the intensity of the fluorescence was practically independent of the pressure.

The quality of the fluorescence was not affected by the pressure, for the same spectrum was obtained at high as at low pressures.

V. The Effect of Temperature.

The temperature of the bulb was varied from the temperature at which the vapor began to fluoresce (the boiling point of anthracene is $351°$ C.) to the temperature at which the glass began to soften (the melting point of the glass bulb is about $1000°$ C.). As the temperature was raised the intensity of the fluorescence diminished. This was the case whether the bulb contained the pure anthracene alone or mixed with an inert gas. Of course, as the temperature was raised, the pressure of the enclosed vapor was increased, so the effect may have been due to this.

VI. The Effect of Varying the Density of the Vapor.

When the amount of anthracene enclosed in the bulb was gradually increased and the vapor density thus correspondingly

increased, it was found that the cone of visible fluorescence, which at first extended completely through the bulb from the point where the exciting light entered to the point where it left, was fore-shortened in the direction of its length until, finally, it was shrunk down almost to the surface where the exciting light entered the bulb. At the same time the intrinsic brightness of the fluorescence was diminished, due, undoubtedly, to the consequent in-crease in pressure.

The foreshortening of the cone of fluorescence means, of course, that the particular radiation which excites the visible fluorescence is completely absorbed out of the incident light before this penetrates very far into a bulb filled with dense anthracene vapor.

The quality of the fluorescence, however, was not affected, as the spectr m photographs for bulbs containing different amounts of anthracene showed.

VII. The Absorption Spectrum.

To obtain the absorption spectrum of the vapor it was found convenient to use a long glass tube in which to enclose the anthracene. This was placed inside a cylindrical iron tube

with a glass window at each end, as shown in Fig. 2.

Fig. 2.
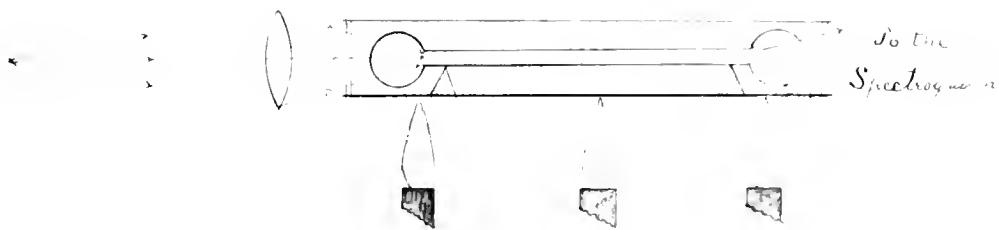
The light from a Nernst filament was focused in the tube at one
end, and, on emerging at the other end, was examined photographically
with the quartz spectrograph.

The photograph (Plate II,1) was taken when the anthracene
vapor in the tube was quite dense. It shows that the pure dense
vapor absorbs continuously from 425$\mu\mu$ to 325$\mu\mu$, the limit set
by the crown glass. When the tubes containing less anthracene,
or the bulbs employed in getting fluorescence, were used the
absorption did not extend so far down towards longer wave-lengths
(Plate II, 2 & 3).

The absorption of the vapor was also studied with a 12.5-foot,
concave Rowland grating, but with the same result. There was

no evidence of lines in either case; the absorption consisted of a continuous region between $325\mu\mu$ and about $425\mu\mu$.

Purified anthracene was used in obtaining the absorption spectra just described. When the commercial Anthracene (Eimer & Amend, 90%) was used, the absorption spectrum obtained (Plate II, 4) was found to be the same as for the pure anthracene with the exception that there was a narrow band at wave-length $452\mu\mu$.

VIII. The Relation between the Exciting Light and the Fluorescence. Stokes' Law.

1. The Carbon Arc as Source.

In the earlier stages of the investigation, when the fluorescent spectrum was excited by the light from a carbon-arc lamp and the photograph taken showed that it consisted of three bands which were somewhat similarly spaced, but farther towards the red, as compared with the three intense cyanogen bands of the arc in that region of the spectrum, it was thought probable that the three cyanogen bands had each excited its own fluorescent band in the anthracene vapor, thus giving rise to the three bands found in the fluorescent spectrum. The fact that sunlight excited the same bands seemed to make this doubtful; but it was not until the work, now to be described, was done, that it was shown that, in all prob-

ability, the entire fluorescence of the vapor excited by light from
the carbon arc was largely due to the strong lines in the head of
the middle one of the three cyanogen bands, the one whose head lies
at wave-length 388.3 μμ.

Two methods were employed in determining the approximate wave-
length of the exciting light.

(a). The first to be tried was what might be called the "method
of exclusion". It consisted in screening off different portions
of the spectrum in turn, by means of properly chosen absorbing
solutions, and observing the effect upon the fluorescence. By
referring to Dr. Uhler's photographs of the absorbing spectra of
various solutions, the following solutions were chosen and found to
answer the purpose:

A.   Nitroso-dimethyl-aniline solution, 2 parts by volume
     of saturated solution to 3 parts of water;

B.   Potassium permanganate solution, 1 part by volume of
     saturated solution to 50 parts of water;

C.   Napthol disulfonic acid solution, 2 parts by volume of
     saturated solution to 5 parts of water.

These solutions were introduced into a glass cell (1 cm.
thick) which was placed in the path of the exciting light between

the condensing lens (see Fig. 1) and the bulb.

When solution A was employed in this manner as an absorbing screen, the anthracene vapor failed to fluoresce. Now, this solution has a stron absorption band extending from $375\mu\mu$ to $480\mu\mu$(see Plate III), while it transmits quite freely on both sides of the band, within the limits set by the glass. It is evident from this that the light which causes the fluorescence in the vapor is located somewhere in the region $375\mu\mu$ to $480\mu\mu$. It is in this region that two of the cyanogen bands are located; the third lies just outside of it towards the ultraviolet.

The solution B is transparent to light of wave length $395\mu\mu$ to $465\mu\mu$, but is quite opaque to the rest of the spectrum in the given region. When this solution was substituted in the cell for solution A, no fluorescence could be observed. This shows that the light producing the fluorescence does not lie between $395\mu\mu$ and $465\mu\mu$, and therefore must lie either in the region $465\mu\mu$ to $480\mu\mu$, or in the region $375\mu\mu$ to $395\mu\mu$, or in both. That it does not lie in the region $465\mu\mu$ to $480\mu\mu$ is probable from the fact that the carbon-arc spectrum is relatively weak in this region. We are then led to conclude that the exciting light lies somewhere between the wave-lengths $375\mu\mu$ and $395\mu\mu$. It is in this region that the strong lines in the middle of one of the three cyanogen

bands are located.

(b). A confirmation of the foregoing results was obtained in the following way: A slit, two condensing lenses and a large crown-glass prism were arranged so as to give a comparatively pure and bright spectrum of the arc. A slitted screen, with the bulb containing the anthracene vapor behind it, was then passed from point to point along through the spectrum. Starting at the red end there was no visible evidence of fluorescence in the vapor until the bulb was brought into that part of the spectrum corresponding to wave-lengths 390 to 375 $\mu\mu$ when it began to fluoresce with the characteristic brilliant blue color, the cone of fluorescence extending entirely through the bulb. When moved on into the region of the cyanogen band whose head is at 359 $\mu\mu$, a dim fluorescence was observed which penetrated only a few millimeters into the bulb. It had played no part, therefore, in the photographs of the fluorescent spectrum previously taken, where the collimator of the spectrograph had been directed towards the center of the bulb.

The slitted screen was now adjusted so as to allow only the light near the head of the cyanogen band at 388.3 $\mu\mu$ to enter the bulb. A photograph of the fluorescence produced was taken which
and continuous regions
gave the same bands ʌ shown in the former photographs (see Plate I).

The slit was then moved so as to admit to the bulb the head of the cyanogen band at 359 $\mu\mu$, and a photograph of the fluorescence was taken. It showed that the spectrum was the same as that excited by the other cyanogen band.

The relative spectral positions of the fluorescence and the exciting lights for the two experiments just described are shown in Fig. 3. The block E_1 represents the spectral width and location of the exciting light in the first experiment and F_1 the general

Fig. 3.

form of distribution of intensity in the fluorescence which it excited in the anthracene vapor, while E_2 and F_2 represent the corresponding quantities in the second experiment. The two curves have been deduced from the photographs and indicate that the fluorescence in the two cases was the same in every way except in absolute intensity.
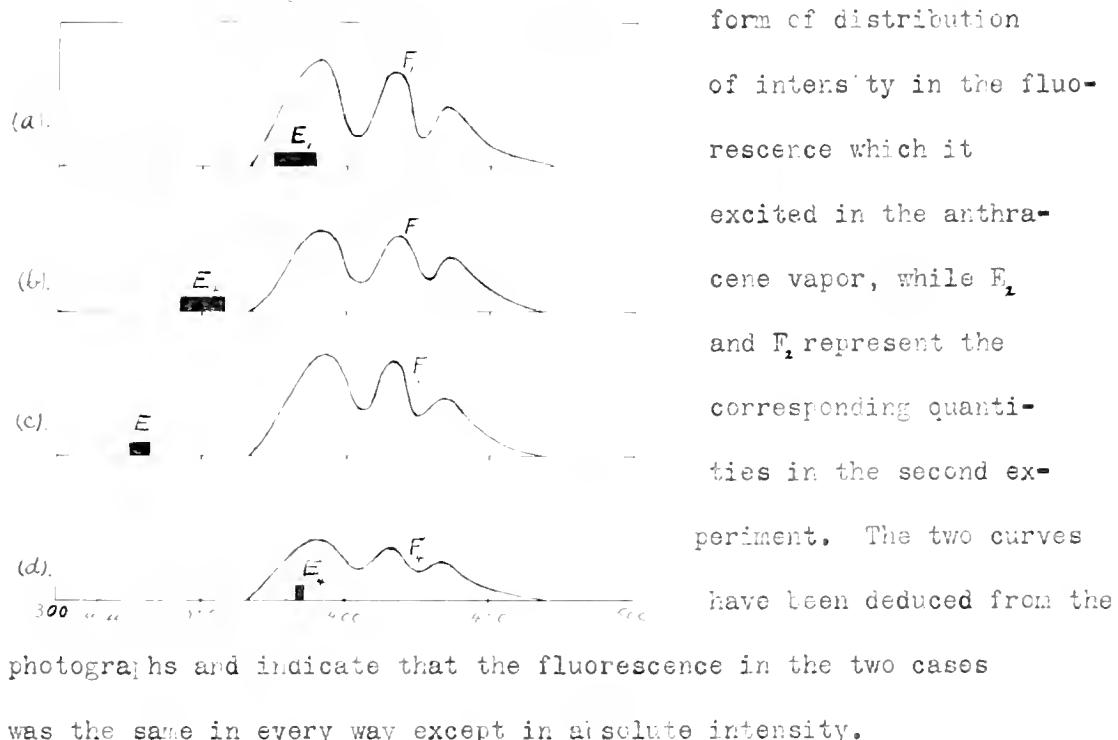
2. The Zinc Arc and Magnesium Spark as Sources.

To obtain further evidence of the relation between the fluo-
rescence and the wave-length of the light which excites it, two
sources were employed which gave regions of exciting light quite
widely separated. The first was the zinc arc, which gives an
isolated group of very intense lines in the region 328 - 335 $\mu\mu$,
just within the ultraviolet limit set by the absorption of the crown-
glass bulb; the second was the magnesium spark, which gives an
intense isolated triplet in the region 383-385 $\mu\mu$, not very far
from the limit towards the red beyond which the light ceases to
have power to excite fluorescence in the anthracene vapor. This
limit was earlier found to be in the neighborhood of wave-length
400 $\mu\mu$.

Between 325 $\mu\mu$ and 400 $\mu\mu$ the arc-spectrum of zinc contains,
besides the group just mentioned, only three very faint lines whose
aggregate intensity is less than 1% of that of the group. If
the zinc arc is used, therefore, to excite the fluorescence
in the anthracene, the exciting light is practically all located
in the region 328 - 335 $\mu\mu$. — When this was done(the zinc arc
being substituted for the carbon arc) and the fluorescence pro-

duced in the bulb was photographed, it was found to give the same
fluorescent spectrum as the carbon arc. The block E_J and the curve
F_J in Fig. 3 respresent respectively the exciting light and the
fluorescence for this case.

In the case of the magnesium spark there are a few faint lines
in the region 325-400$\mu\mu$ besides the triplet mentioned, but their
aggregate intersity is negligible in comparison with that of the
triplet, so that practically all of the exciting light from a pure
magnesium spark is in the region 383 - **385**$\mu\mu$. It was found,
however, that the electrodes used contained zinc as an impurity.
In order to screen off the lines due to the zinc the solution C
(see $\S$ VIII, 1) was used as an absorbing screen. It is opaque
to ultraviolet light from 360$\mu\mu$ on out beyond 325$\mu\mu$, and there-
fore to the group of zinc lines at 328-335 $\mu\mu$. ▬ When the mag-
nesium spark, as thus screened, was used as the source and the
fluorescence excited was photographed, it was found to give the
same spectrum as the carbon and zinc arcs. The block E and the
curve F in Fig. 3 represent respectively the exciting light and
the fluorescence for this case.

In connection with the results given above it should be
remembered that the anthracene vapor used absorbs continuously from
about 400$\mu\mu$ to some point beyond 325 $\mu\mu$.

3. Stokes' Law.

It is evident from the foregoing facts that Stokes' Law, which states that the fluorescent light is of longer wave-length than the light which excites it, is not strictly true in the case of anthracene vapor; for in at least two cases (a and d in Fig. 3) part of the fluorescent light is of shorter wave-length than the corresponding exciting light. In a general sense, however, the law may be considered as fairly representing the facts, since the fluorescent spectrum as a whole is of longer wave-length than the exciting light.

4. Discussion of Results.

We are led to conclude from the foregoing facts, (a) that the fluorescence of anthracene vapor is excited by light situated anywhere in the ultraviolet region of absorption of the vapor, and (b) that the character of the fluorescence is entirely independent of the source and wave-length of the light which excites it.

If we assume that the fluorescence is produced by a system of electrons within the molecule, then in order to account for the fluorescent spectrum of anthracene vapor, which as we found was composed of three bands superposed upon a continuous spectrum, we may consider either that the electrons corresponding in period to the three bands are more numerous than those which give rise to the

weaker, continuous parts of the fluorescence, or that these electrons are set in more violent vibration; also, that the system of electrons is so intimately connected in its parts that when disturbed in any manner, be it direct or through an intermediary "luminophore", they are <u>all</u> set in vibration. If the disturbance of the system takes place through an intermediary "luminophore",[9] as seems more probable, then this luminophore undoubtedly consists of a connected system of electrons whose periods correspond to those of the absorption spectrum of the vapor.

### IX. <u>The Fluorescence and Absorption of Phenanthrene Vapor, the Isomer of Anthracene Vapor.</u>

Phenanthrene is a substance which has the same chemical composition, $C_{14}H_{10}$, as anthracene, but a slightly different structural composition, as the following figure shows:

Figure 4.

Anthracene   Phenanthrene.

9. W. Kauffmann, Ber. d. Phys. Gesell. 21, 375, 1905.

The only difference in structure according to this is in the manner in which the four groups or radicals are linked together.

When the fluorescent spectrum of pure phenanthrene vapor was photographed (Plate IV), it was found to consist of the same bands as that of anthracene, but with an additional band at $360\mu\mu$.

Its absorption spectrum was photographed and found to be the same as that of the anthracene vapor.

It would seem from these facts that there is an intimate connection between the fluorescence of the vapors of the two substances, undoubtedly due to their common chemical composition and similar structural composition. Just what gives rise to the extra band in the fluorescent spectrum of phenanthrene vapor is not apparent.

X. Summary.

The following is a summary of the results of this investigation:

(1). The fluorescent spectrum of anthracene vapor consists of three bands at 390, 415 and $432\mu\mu$ superposed upon a continuous region extending from $365\mu\mu$ to $470\mu\mu$. There is no evidence of lines. - The absorption spectrum extends continuously from about $400\mu\mu$ to some point beyond $325\mu\mu$.

(2). The presence of inert gases in the vapor does not affect the fluorescence, so long as the pressure is below an atmosphere. But such gases as oxygen, chlorine and sulphur dioxide, which at high temperatures react chemically with

anthracene, almost completely extinguish the fluorescence at ordinary
pressures.

(3). The intensity of the fluorescence decreases as the pressure
of the gas enclosed with the anthracene is increased. It is not
marked, however, at pressures lower than an atmosphere. — The
quality of the fluorescence is not affected by a change in
pressure.

(4). Increasing the density of the fluorescing vapor has no
effect upon the quality of the fluorescence, but diminishes its
intensity slightly.

(5) The fluorescence of anthracene vapor may be excited by light
located anywhere within the ultraviolet region of absorption
of the vapor.

(6). The same fluorescent spectrum is produced independent of
what the source or wave-length of the exciting light may be,
provided the condition noted in (5) is observed.

(7). There is an intimate connection between the fluorescence
of anthracene vapor and its isomer, phenanthrene vapor.

This investigation was begun at the suggestion and has been
carried out under the direction of Professor R. W. Wood, to whom I
wish to extend my thanks for the interest which he has shown and the

encouragement and help which he has given me in the course of the
work.   I wish also to express my gratitude to Professor J. S. Ames
for his unfailing courtesy and kindness.
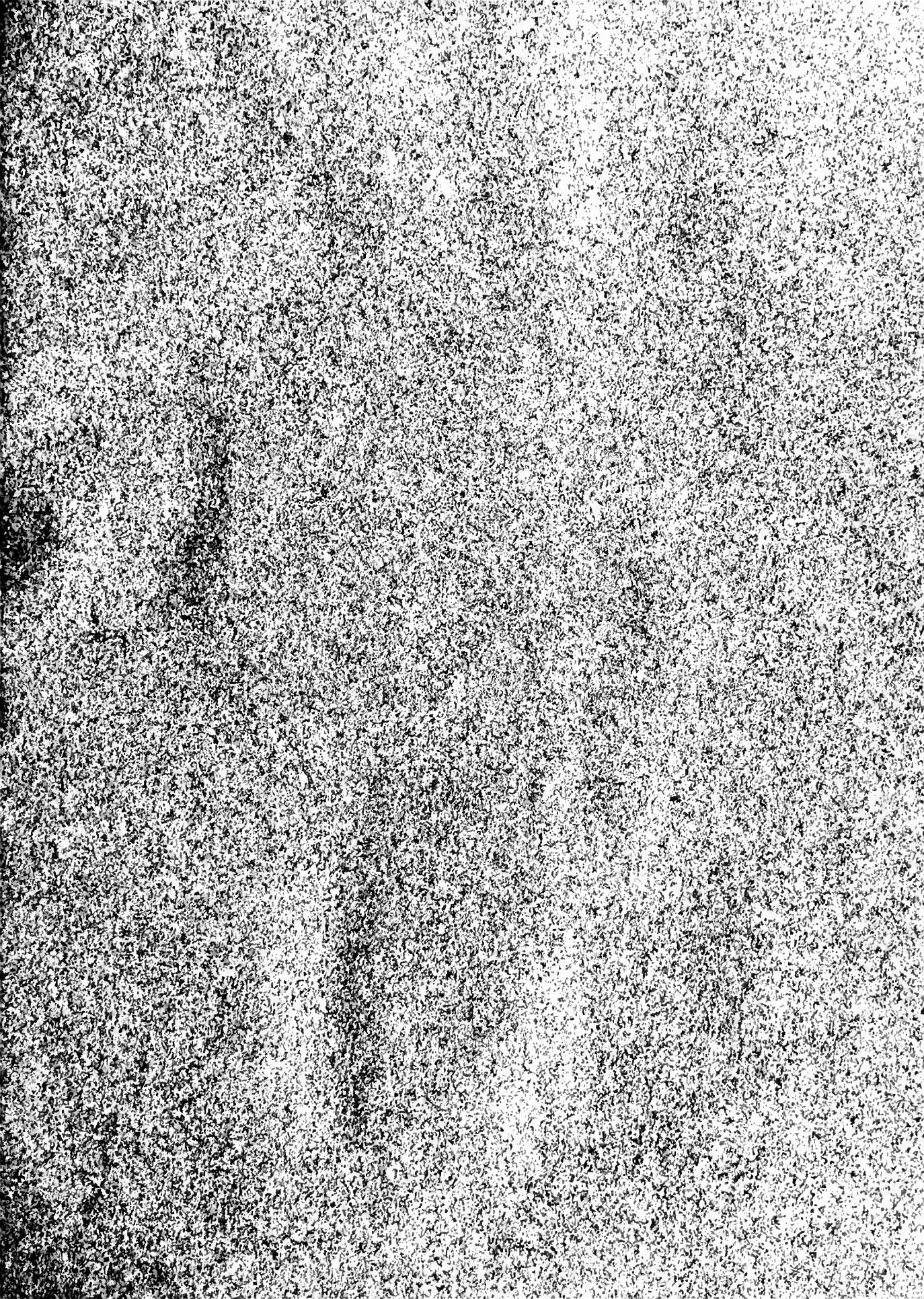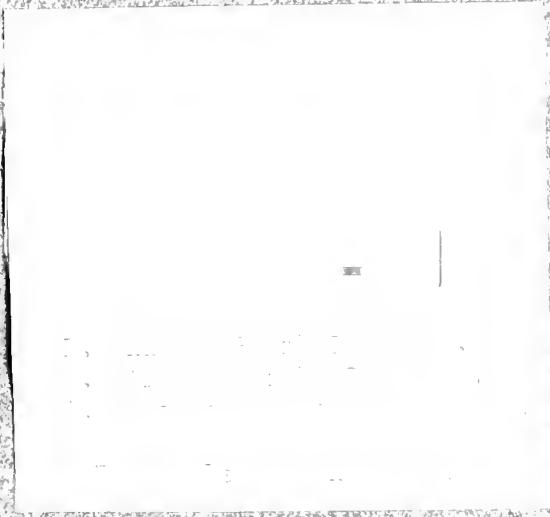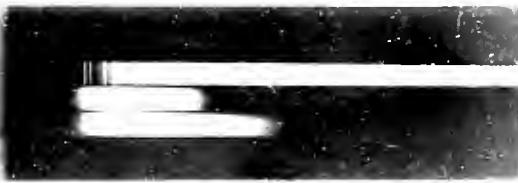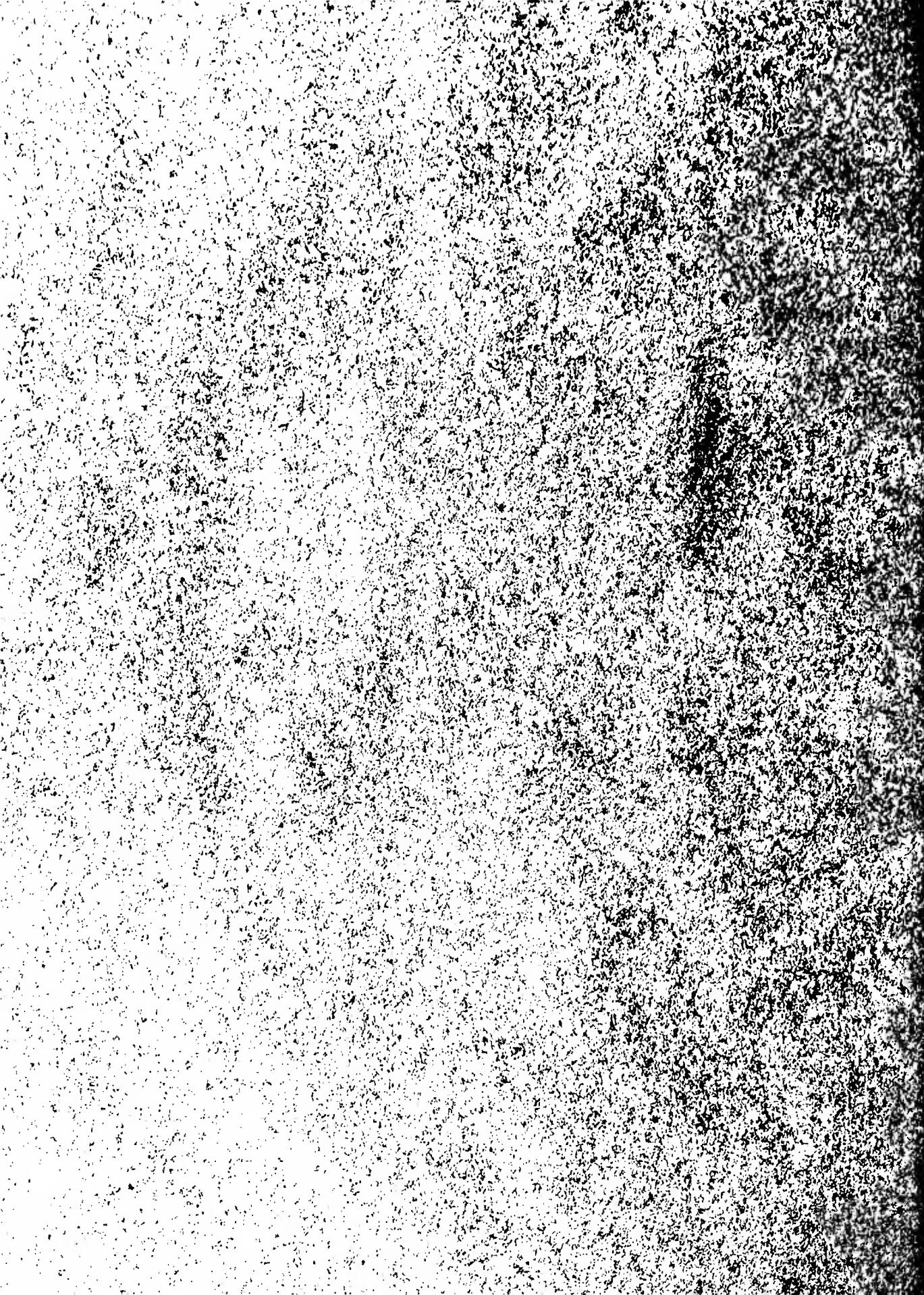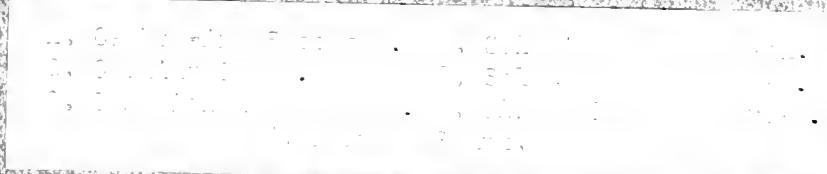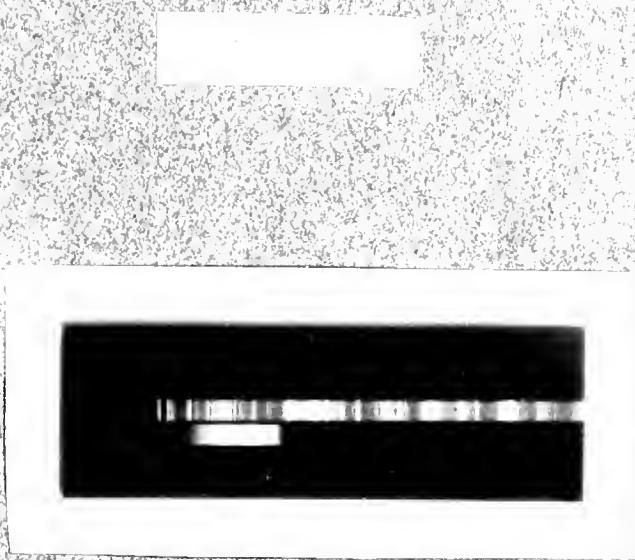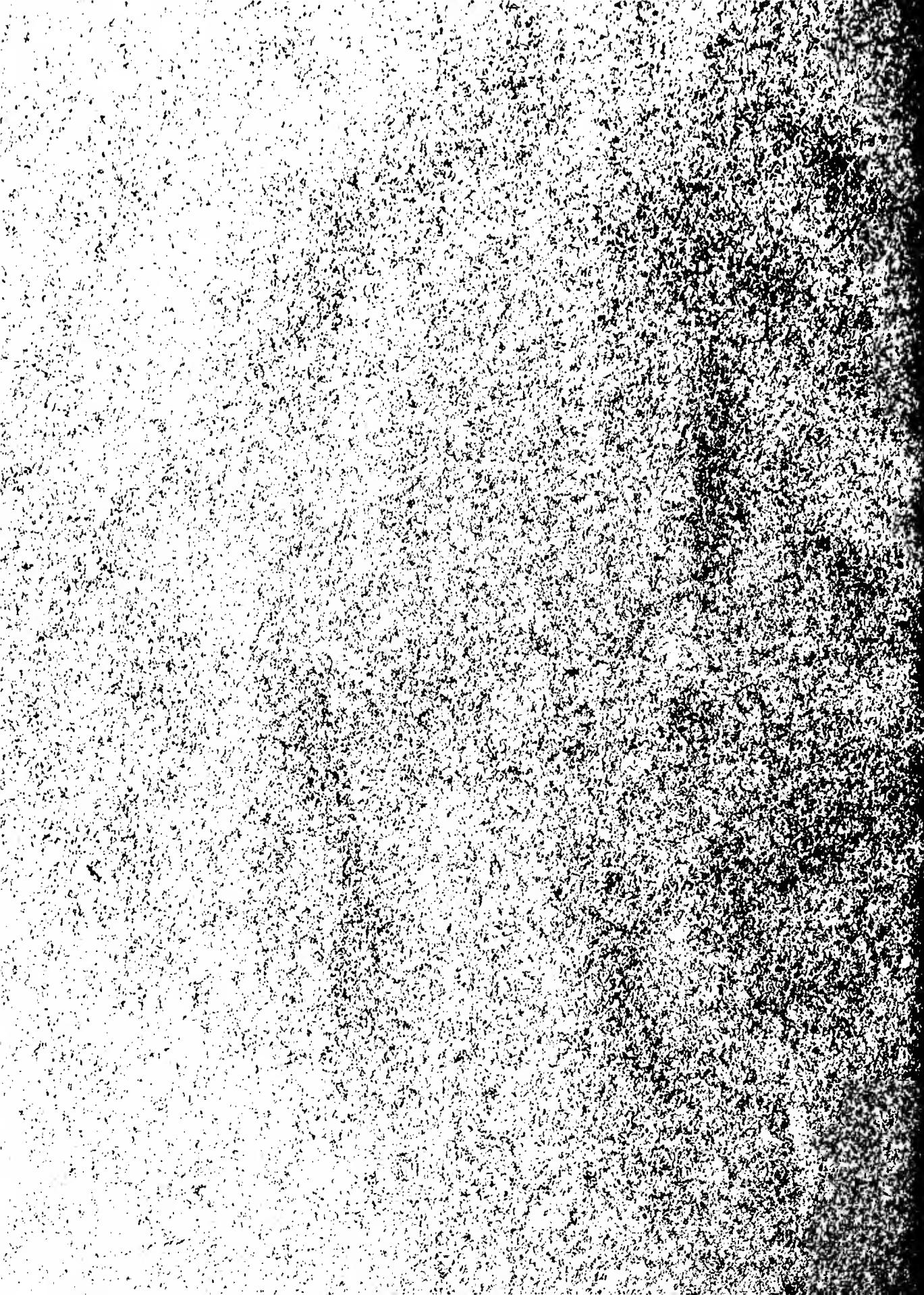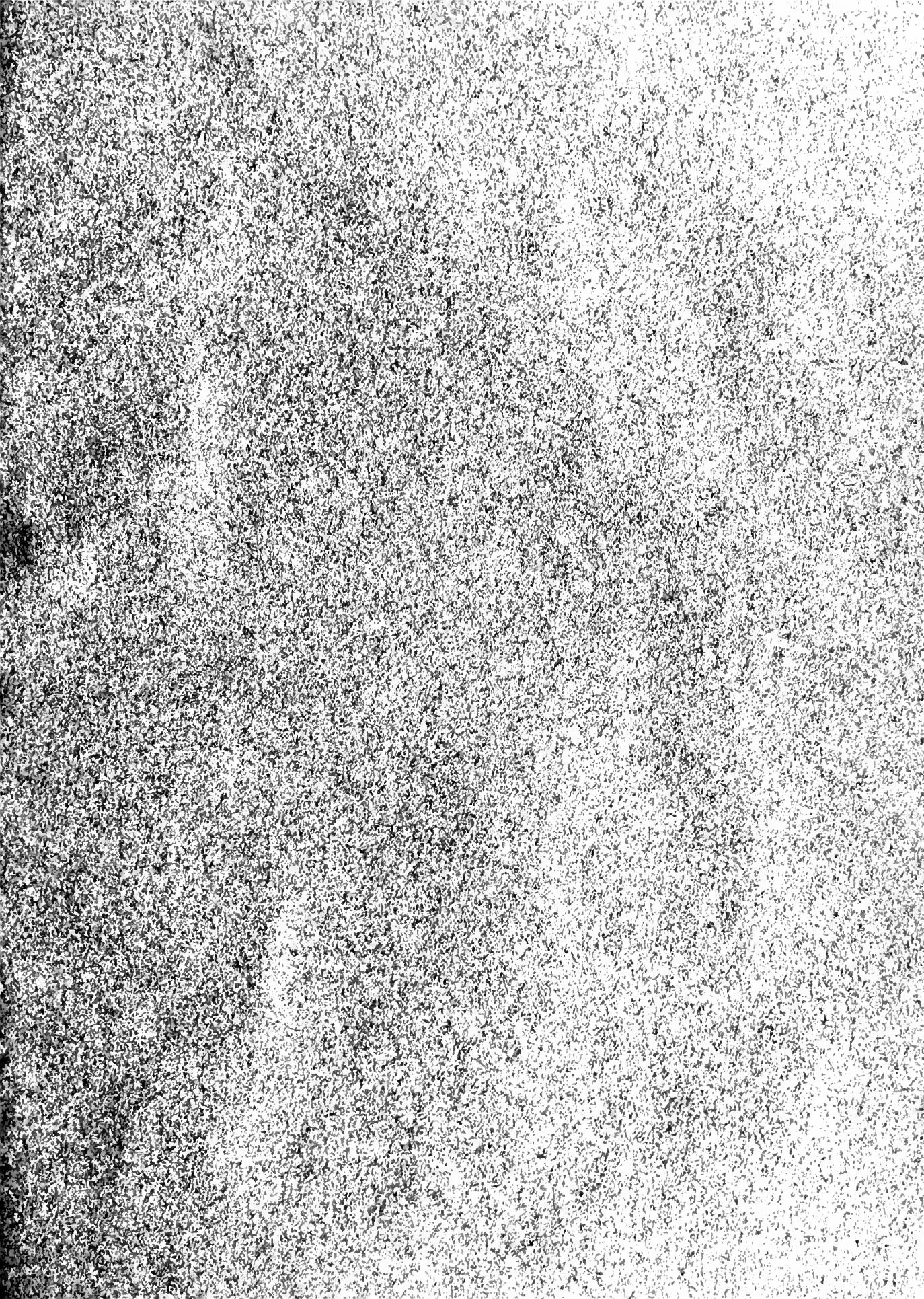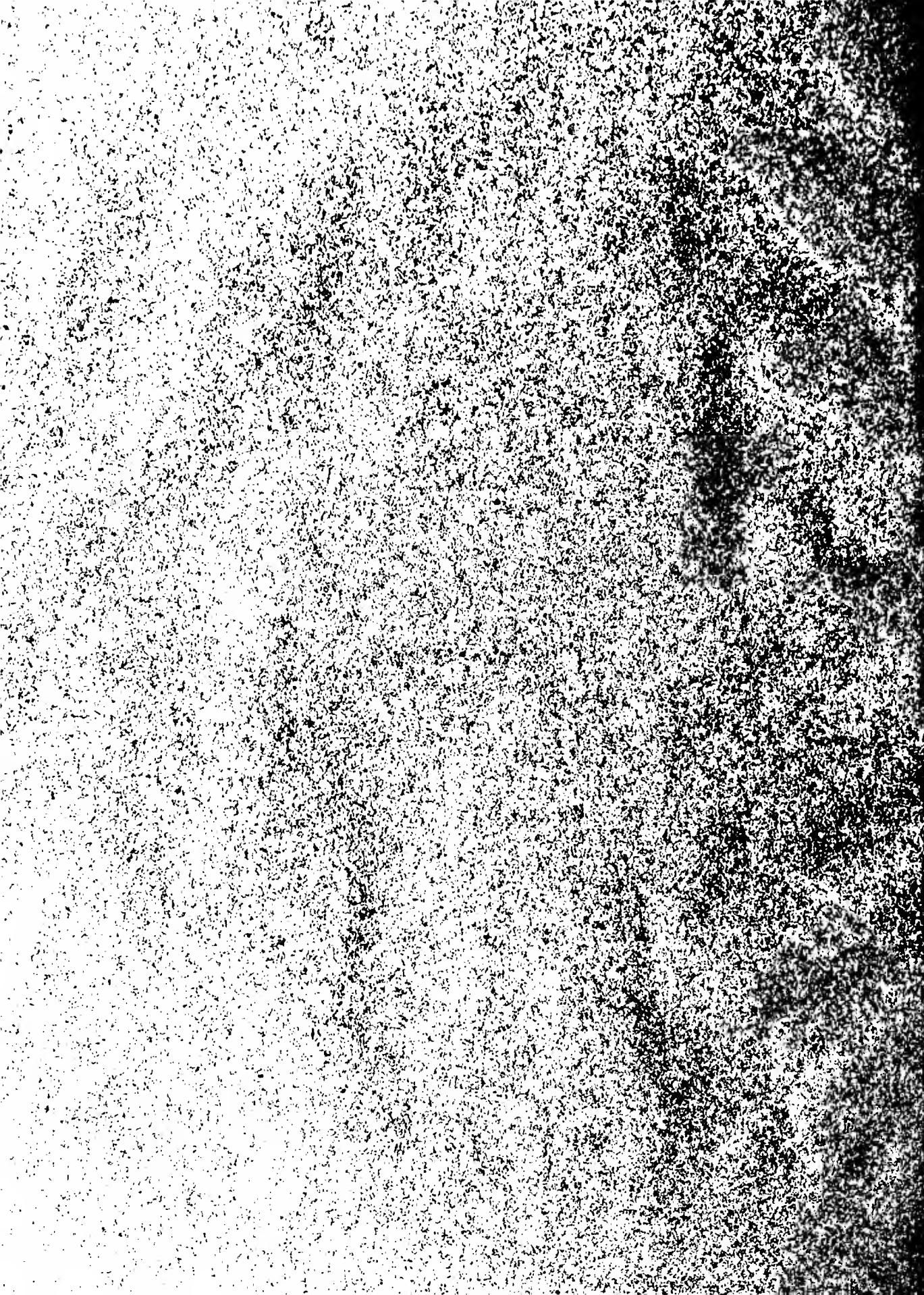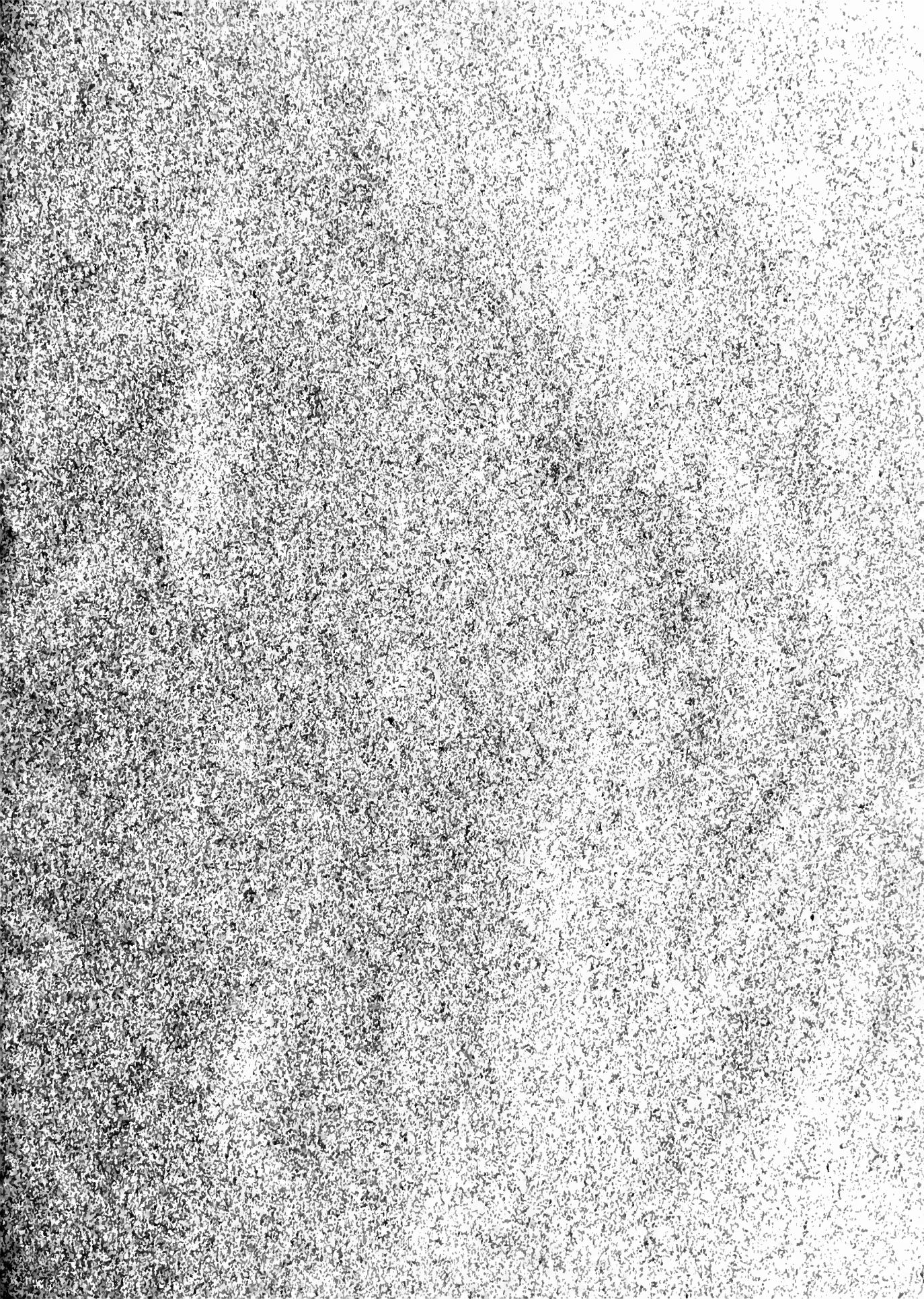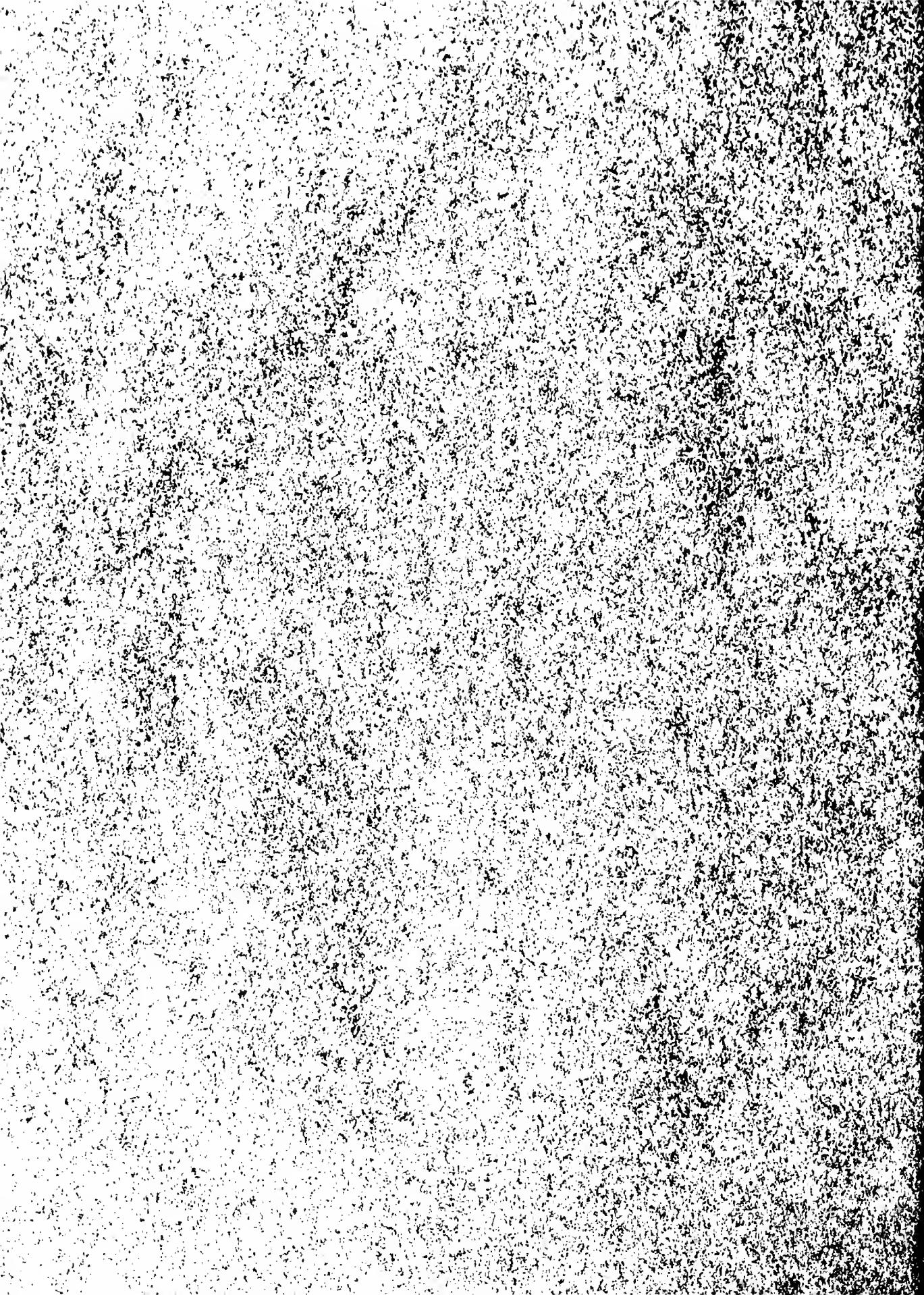
BIOGRAPHY.

Thomas Sidney Elston was born in the town of Woodland, Sacramento Valley, California, on the sixteenth of December, 1872. He received his preparatory education at Hesperian College, Woodland, Cal. Between the date of his graduation from this school and his matricualtion in 1895 at the University of California at Berkeley he spent three years in an accountant's office. He received his bachelor's degree from the Colleges of Natural Science at the university in 1899. The following year he taught physics in the San Diego High School, Cal. The second year he was called to take charge of the same work in the High School at Berkeley, in which he continued until he came to the Johns Hopkins University as Research Assistant to Professor R. W. Wood. Since that time he has been pursuing graduate study in Physics in the Johns Hopkins Physical Laboratory under Professors Ames and Wood. His first and second minors have been respectively Mathematics under Dr. Cohen and Physical Chemistry under Dr. Jones.